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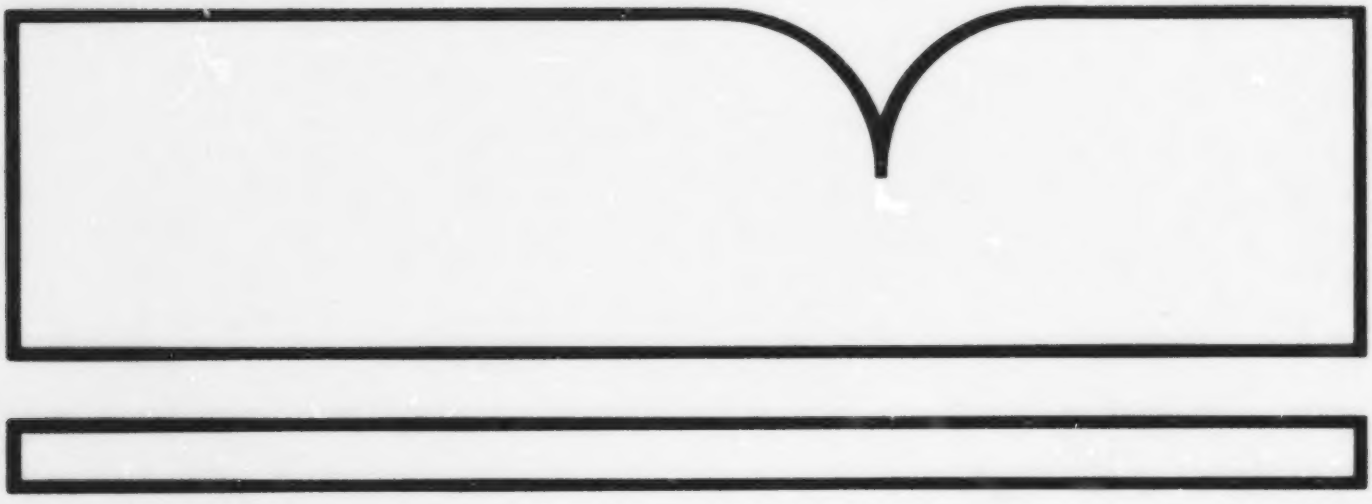

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LABORATORY AND FIELD EVALUATION OF THE SEMI-VOST METHOD

VOLUME I

by

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An initial laboratory and field evaluation study has been completed which assessed the performance of the Semi-Volatile Organic Sampling Train Method (Semi-VOST) for measuring concentrations of principal organic hazardous constituents (POHCs) with boiling points greater than 100°C that are emitted from hazardous waste incinerators. A draft formulation of the methodology was tested through an experimental laboratory program to evaluate method performance characteristics. The program consisted of: (1) determination of minimum compound detection limits; (2) simulation of a flue gas stream to determine the impacts of water vapor, SO_2, NO_x, and HCl on sampling; and (3) determination of precision and bias for the sample preparation and analytical elements of the method. Results of the simulation study are reported for 12 test compounds (POHCs) representing a range of physical and chemical properties which could affect sample train collection and recovery performance. Three of the test compounds were selected for further investigation to evaluate method precision and bias under field conditions through the use of four simultaneously-operating Semi-VOST trains. Project results are presetned in Volume I along with recommendations on elements of the method requiring further research. Volume II includes appendices giving detailed descriptions of the method formulation, laboratory, and field studies along with quality assurance data.

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ABSTRACT

An initial laboratory and field evaluation study has been completed which assessed the performance of the Semi-Volatile Organic Sampling Train Method (Semi-VOST) for measuring concentrations of principal organic hazardous constituents (POHCs) with boiling points greater than 100°C that are emitted from hazardous waste incinerators. A draft formulation of the methodology was tested through an experimental laboratory program to evaluate method performance characteristics. The program consisted of: (1) determination of minimum compound detection limits; (2) simulation of a flue gas stream to determine the impacts of water vapor, SO_2, NO_x, and HCl on sampling; and (3) determination of precision and bias for the sample preparation and analytical elements of the method. Results of the simulation study are reported for 12 test compounds (POHCs) representing a range of physical and chemical properties which could affect sample train collection and recovery performance. Three of the test compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were selected for further investigation to evaluate method precision and bias under field conditions through the use of four simultaneously-operating Semi-VOST trains. Cylinder gas standards of each compound were blended and dynamically spiked into paired sample trains for determining method bias. Estimates of bias are presented for toluene and 1,1,2,2-tetrachloroethane. Method precision for chlorobenzene is calculated from unspiked sample train results which also included distributive volume experiments to determine sample train breakthrough of POHCs. Project results are presented in Volume I along with recommendations on elements of the method requiring further research. Volume II includes appendices giving detailed descriptions of the method formulation, laboratory, and field studies along with quality assurance data.

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SECTION 1
INTRODUCTION

The Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976 (RCRA), requires that the Environmental Protection Agency establish a national regulatory program to ensure that hazardous wastes are managed in a manner which does not endanger human health or the environment. The statute requires EPA to promulgate performance standards for hazardous waste management. Included in the regulations that have been promulgated are provisions for waste disposal by incineration and requirements that hazardous waste incinerators be so operated that the principal organic hazardous constituents (POHC's) are destroyed and/or removed with a minimum efficiency of 99.99 percent. To determine destruction and removal efficiency (DRE), EPA has designated the Semi-Volatile Organic Sampling Train Method (Semi-VOST) as the method for measuring concentrations of POHC's with boiling points greater than 100°C that are emitted from hazardous waste incinerators.

The Quality Assurance Division of the Environmental Monitoring Systems Laboratory at Research Triangle Park, North Carolina has a program to evaluate and standardize EPA source test methods. While participating in this program, Radian Corporation has undertaken an evaluation of the Semi-VOST Method, which is the subject of this report. The objectives of the program were the following:

- assemble and refine a draft formulation of the Semi-VOST sampling and analysis methodology;
- select a series of Appendix VIII test compounds for method evaluation based on the characteristics of incinerability, water solubility, and adsorption strength on XAD-2® resin;
- design and conduct an experimental laboratory program to evaluate method performance characteristics in terms of minimum compound detection limits, sampling flow rate and volume, and

the formation of artifact compounds during the sampling of a simulated flue gas stream containing water vapor, SO_2, NO_x, and HCl;

- determine precision and bias attributable to each of the sample preparation steps and the final GC/MS analysis step;
- design, construct, and evaluate the performance of a dynamic spiking system for determining method bias using experimental field data; and
- carry out a field test study at a hazardous waste incineration facility to evaluate method precision and bias, and the potential of POHC sample train breakthrough.

The evaluation was conducted in several stages. The initial effort focused on defining a formulation of the Semi-VOST method. The method is presented in detail in Appendix A and is summarized in Section 4. A laboratory study was then conducted to determine the method's precision and bias under carefully controlled conditions. This work is summarized in Section 5 of the report with supporting details presented in Appendices B, C, and D. The final stage of this investigation involved evaluating the method in a field test. These results are summarized in Section 6 of the report, and supporting details are presented in Appendices E, F, and G. Conclusions and recommendations from this work are presented in Sections 2 and 3, respectively.

SECTION 2
CONCLUSIONS AND FINDINGS

Several major conclusions and findings can be drawn from the Semi-VOST evaluation conducted to date.

- Method precision and bias are compound-specific and cannot be generalized for all classes of chemicals. Laboratory experiments demonstrated that method precision and bias are related to the distribution and recovery of a particular POHC throughout the components of the sampling train. Sample distribution and recovery of a POHC is related to its boiling point, water solubility, and chemical function.

- A method precision of 19.9 percent for chlorobenzene was calculated from a field test data set representing seven degrees of freedom which resulted from a series of paired, unspiked Semi-VOST trains sampling the emissions from a hazardous waste incinerator. The contributions of sampling, sample preparation, and GC/MS analysis to the total variance were 78.5, 1.4, and 20.1 percent, respectively.

- The dynamic spiking concept was demonstrated as a viable approach for determining method bias in field evaluation studies.

- A preliminary estimate of method bias of -13 percent for toluene was calculated from field test data obtained using the dynamic spiking system.

  - The 87 percent recovery of toluene from the field test data compares favorably with the mean recovery of 91 percent measured from the laboratory baseline performance test of the dynamic spiking apparatus.

  - The identification of toluene in the methylene chloride recovery solvent returned from the field necessitates analysis of additional sample fractions from the test to confirm the toluene bias estimate.

- A preliminary estimate of method bias of -16 percent was calculated for 1,1,2,2-tetrachloroethane from Run 1.

- The 84 percent recovery of 1,1,2,2-tetrachloroethane is in agreement with the 85 percent value from the baseline dynamic spiking test.

- The Run 2 data for 1,1,2,2-tetrachloroethane were not included in the bias estimate because of suspected problems with the concentration equilibrium of the compound in the dynamic spike.

- Compounds adsorbed on XAD-2® resin exhibited better precision and recovery than compounds collected in the condensate and impingers.

- The field test distributive volume experiments demonstrated that chlorobenzene did not break through the sample train and the retention volume for chlorobenzene was not exceeded. Thus, the current formulation of the Semi-VOST method is adequate for chlorobenzene.

- Test compound recoveries were not affected by either simulated flue gas variations in compound concentration by HCl, SO_2, or water vapor, or by variations in sample flow rate and volume.

- Increases in generated flue gas NO_x levels were associated with decreases in the recoveries of 1,4-dioxane, urethane, and phenol.

- For toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane, laboratory experiments showed that the precision of the resin extraction and concentration steps was not significantly different from the precision of the concentration step alone. However, the precision of the separatory funnel extraction and concentration steps was significantly poorer than either the precision of the concentration step alone or the resin extraction and concentration step.

- For chlorobenzene, toluene, and 1,1,2,2-tetrachloroethane, no significant losses were detected when the K-D concentrate was reduced from 5 mL to 2.5 mL using an inert gas for blowdown.

- When available, the use of surrogate standards during sample preparation and analysis is desirable to obtain accurate compound recoveries.

SECTION 3
RECOMMENDATIONS

Based on the results of the method evaluation studies presented in this report, the following recommendations are made for further investigation.

- Method bias and precision have been shown to be compound specific. An investigation should be conducted to determine if Appendix VIII compounds could be aggregated according to properties such as water solubility, chemical similarity or adsorption strength (retention volume) on XAD-2 to provide estimates of method precision and bias for compound categories.

- Pyridine, pentachlorophenol and resorcinol exhibited poor recoveries during the flue gas generator experiments. Preliminary studies have indicated that compound losses may be attributed to either chromatographic properties, poor solvent extraction, or compound reaction in the aqueous components of the sampling train which become acidified during sample collection. Also the low recovery of pentachlorophenol may have been due to loss within the flue gas generator. Further laboratory studies are warranted to clarify these observations and to develop simplified screening procedures to demonstrate the applicability of the method's sample preparation (extraction) and analysis (GC/MS conditions) steps to other Appendix VIII compounds or classes of compounds.

- The recovery losses of urethane, phenol, and 1,4-dioxane associated with NO_x flue gas generator levels should be studied using solutions to simulate condensate and impinger contents for evaluating compound reactivity with NO_x. Findings could then be used to plan a second field evaluation of the method which includes POHC artifact formation study objectives.

- The particulate filters from the Semi-Vost samples collected during the field test program were stored and solvent extracted for later analysis. The extracts should be analyzed for semi-volatile compounds in preparation for future studies to evaluate POHC-particulate matter interactions during sample collection.

- The preliminary estimates of method bias for toluene and 1,1,2,2-tetrachloroethane should be finalized by analyzing the remaining sample fractions from field test Runs 1 and 2. The presence of toluene in the methylene chloride rinse solvent should also be accounted for.

- The dynamic spiking system for determining method bias should be redesigned to improve its reliability in the field. The use of a stable, single gas mixture containing multiple components would simplify operation and delivery of a dynamic spike to two simultaneously-operating Semi-Vost trains. Stable, isotopically-labeled POHCs would be desirable spiking components as it is unlikely that they would be present in the flue gas.

- The existing field study GC/MS analytical data set for unspiked sampling runs should be re-examined to determine if additional flue gas organic compounds could be used to evaluate sample train breakthrough.

- Future field method evaluation studies should include the addition of spiked waste feed materials to permit measurement of method precision and sample train breakthrough for several pre-determined compounds contained in the spiked waste.

SECTION 4
METHOD FORMULATION

The basic Semi-VOST sampling method evaluated in this study is cited in Reference 1. The original method formulation contained no analytical protocols but included several sections that were discretionary or that required clarification. Therefore, prior to laboratory experimentation, a refinement in the formulation was developed by surveying members of the technical community who had experience in the use of the Semi-VOST method. A list of companies contacted in this survey is included in Appendix A. Based on the survey responses, a working copy of the method was drafted to encompass both sampling and analysis procedures. Details of the method can be found in Appendix A with changes and/or additions to the formulation highlighted on pages A-1 and A-2.

In the application of Semi-VOST, gaseous and particulate components are isokinetically withdrawn from an emission source and collected in a multicomponent sampling train. Key elements of the train include a high-efficiency particulate filter and a packed bed of a porous polymeric adsorbent resin (XAD-2®). The filter is used to separate stack gas particles from gaseous substances which are then adsorbed on XAD-2®. As a collection sorbent, XAD-2®, a polystyrene-divinylbenzene copolymer, has the advantage of high surface area (300 m^2/g) with an average pore volume of 90 Å which affords the capacity for collection of semi-volatile compounds. Following sample collection, the train components are extracted with solvent, concentrated, and identified/quantified using high resolution gas chromatography coupled with low resolution mass spectrometry.

After return of the samples to the laboratory, all fractions are spiked with surrogate standards prior to extraction, concentration, and analysis. The use of surrogates provides a measure of the efficiency of

the sample preparation procedures. In the sample analyses, an examination of surrogate recovery is used to qualify and possibly correct the analytical results. For example, poor or variable surrogate recovery would suggest difficulties with sample preparation/analysis as opposed to incinerator operation. The spiking compounds should be the stable isotopically-labeled analogs of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis. Potential surrogate spiking compounds include: deuterated naphthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon 13-labeled pentachlorophenol.

The condensate knockout trap solution is spiked with the surrogates, transferred to a separatory funnel, acidified, and extracted with methylene chloride. The aqueous phase is made alkaline and re-extracted with methylene chloride. This procedure is used to optimize the recovery of POHCs with different functional groups. The condensate may contain compounds which show great water solubility and low organic solvent solubility. The methylene chloride solutions are combined in a Kuderna-Danish (K-D) evaporator/concentrator and reduced in volume usually to less than 10 mL and a standard is added for quantitation by gas chromatography coupled with mass spectrometry (GC/MS). Impinger contents are extracted with methylene chloride under both acidic and basic conditions and then concentrated. The methylene chloride/methanol rinses of the probe and filter housing are prepared by spiking with surrogate standards and adding sufficient water to a separatory funnel to force methylene chloride to become immiscible with water and form two phases. The XAD-2® resin is spiked with surrogate standards and transferred with the filter to an all-glass Soxhlet extraction thimble. The module is rinsed with methylene chloride, the solution is added to the Soxhlet, and extraction is conducted for 16 hours.

Analysis is performed by GC/MS using fused silica capillary GC columns. The mass spectrometer is operated in a full (40 to 450 daltons) scanning mode. For most purposes, electron ionization (EI) spectra are

collected since a majority of the potential POHCs give reasonable EI spectra. Also EI spectra are compatible with the NBS Library of Mass Spectra and other reference data which aid in identification.

For quantitation by GC/MS, each sample fraction is spiked with a known amount of an internal standard prior to analysis. The response ratio of the internal standard to each compound of interest in the sample is then compared to a similar ratio established with a calibration curve.

SECTION 5
LABORATORY EVALUATIONS

When evaluating a complex sampling and analytical procedure such as the Semi-VOST method, it is advantageous to obtain as much method performance information as possible before attempting field evaluation studies. Properly-designed laboratory experiments which simulate field sample stream environments can provide data to determine if the execution of the method is in control and to uncover undesirable, determinant characteristics which could then be remedied by modifying the method prior to use in the field.

A laboratory program consisting of three stages was designed and implemented to provide an initial estimate of method precision and bias and to investigate method interferences. The initial portion of the laboratory program involved the selection of compounds to test the limits of the method and for the determination of minimum detection limits (MDL) of the GC/MS. Compound selection was followed by a series of simulated flue gas generation experiments to identify external effects of the sampling environment which would affect the analytical results, and to evaluate the overall method precision and bias. Finally, a series of experiments was conducted to determine specifically the precision and bias of the laboratory preparation and analytical portions of the method.

SELECTION OF TEST COMPOUNDS

The criteria for compound selection were established to evaluate the ability of the method to detect POHCs that: (1) are difficult to incinerate, (2) are soluble in water, (3) have a wide range of boiling points, and (4) have different chemical functional groups.

Based on these criteria, 12 compounds were selected and are presented in Table 1. These compounds represent a range of boiling points from 102°C (1,4-dioxane) to 310°C (pentachlorophenol). Highly-halogenated waste feed components are materials which are difficult to incinerate because of limited C-H bonding. Since XAD-2® was selected as the sorbent resin for the Semi-VOST method because of its ability to adsorb trace organics from both gas phase and aqueous media, a number of water-soluble test compounds were selected to determine the recovery of POHCs from aqueous-scrubbed flue gases. This sampling environment would produce a large volume of condensate passing through the sorbent module. Additional compounds were selected for study which had a range of boiling points within the applicable limits[1] of the method (>100°C). Consideration was also given to challenging the sample extraction elements of the method with both polar and non-polar test compounds.

Initial experiments were conducted to determine the minimum detection limit (MDL) for each of the 12 compounds combined in a solution of methanol. The MDL data were needed to determine appropriate compound spiking levels for generator experiments. The analyses were performed using GC/MS with the statistical method of Glaser, et al.[2] (modified as given in Appendix D), for measuring precision at successive iterations of component concentrations approaching the MDL. Results of the MDL calculations are presented in Table 1.

FLUE GAS GENERATOR EXPERIMENTS

Laboratory experiments were designed to simulate a flue gas environment. Parameters were evaluated which were expected to affect method performance and included: flue gas water vapor, POHC concentration, sample volume and flow rate, and the presence of HCl, SO_2, and NO_x. Determining method performance for sampling streams containing SO_2 and NO_x was of interest because of the potential for sulfonation and/or nitration of XAD-2® or the collected POHCs. These reactions could either alter the adsorptive capacity of the resin for POHCs, create artifacts by fragmenting the resin's cross-linked chemical structure, or promote compound degradation. Details on the design and operation of the generator are presented in Appendix B.

TABLE 1. MINIMUM DETECTION LIMIT (MDL) FOR GC/MS ANALYSIS OF TEST COMPOUNDS IN METHANOL

Selection criteria	Test compound	Boiling point, °C	MDL ng/μL
Incinerability	1,1,2,2-Tetrachloroethane	146	0.25
	Pentachlorophenol	310	4.2
	Hexachloroethane	(sublimes)	0.90
Water solubility	Urethane	180	10.0
	Pyridine	115	8.5
	1,4-Dioxane	102	7.0
Boiling point	Naphthalene	218	0.32
	Chlorobenzene	132	0.37
	Toluene	110	1.9
Chemical functionality	Phenol	182	5.0
	Nitrobenzene	211	1.1
	Resorcinol	280	7.3

Table 2 provides a listing of the variables addressed in the study. Table 3 outlines the test matrix conditions based upon a one-half replicate of a 2^5 factorial experimental design. The operating conditions presented in Table 3 are listed in terms of (1), ab, cd, ae, abcd, etc., as given in the design. The symbol "(1)" represents Level I of all five independent operating variables. Symbol "ab" represents Level II of Variables A and B, and Level I for Variables C, D, and E.

A summary of the results for the flue gas generator studies is given in Table 4 in which the data are expressed as mean percent recoveries for the baseline runs (Runs 1 and 2) and the 16 separate sets of operating conditions. Runs 1 and 2 were initial experiments in which the 12 test compounds were added at the 10 MDL level to a clean air stream. The gas stream was sampled by two Semi-VOST trains "A" and "B." These tests were used to provide an indication of method performance in the absence of generator variables. The surrogate recoveries from the XAD-2® sample fractions are given for comparison with the corresponding sample train compound recoveries from the resin. The remainder of the tests were carried out by collecting samples over the range of test conditions which included the addition of SO_2, NO_x, HCl, and moisture. The percent recovery for each compound for each set of experimental conditions is presented in Appendix B.

The results summarized in Table 4 show that 8 of the 12 test compounds, excluding pentachlorophenol, pyridine, urethane, and resorcinol, have mean recoveries between 81 and 111 percent for all test conditions. The recovery for resorcinol ranged from 0 to 23 percent while the recovery for pentachlorophenol ranged from 0 to 600 percent. Consistently poor recoveries could be due to compound pyrolysis, loss within the flue gas generation system and/or sample loss during sample work-up (i.e., strong affinity of resorcinol for water), and analysis (accumulation of pentachlorophenol in the GC system with intermittent release). Preliminary laboratory experiments have confirmed the poor solvent extraction of resorcinol collected in the sample train. Also the low recovery of pentachlorophenol may have been due to loss within the flue gas generator. Of the remaining two test compounds, pyridine and urethane exhibited either poor or variable recoveries under all

TABLE 2. SAMPLE GENERATION VARIABLES

Variable	Level I	Level II
A	Low moisture	High moisture
	High SO_2 (~750 ppmv)	Low SO_2 (~50 ppmv)
	High HCl (~1,000 ppmv)	Low HCl (~50 ppmv)
B	Low NO_x (~250 ppmv)	High NO_x (~1,000 ppmv)
C	Low hydrocarbon concentration (~3 MDL)	High hydrocarbon concentration (~10 MDL)
D	Small sample size (~0.6 m^3)	Large sample size (~14 m^3)
E	Low sample flow rate (~0.0028 dscm/min)	High sample flow rate (~0.021 dscm/min)

TABLE 3. OPERATING LEVELS FOR A 1/2 REPLICATE OF A 2^5 FACTORIAL EXPERIMENT*,†

Block 1	Block 2
(1)	ac
ab	bc
cd	ad
ae	bd
be	ce
abcd	de
acde	abce
bcde	abde

* Reference. Cochran, William G. and Gertrude M. Cox, "Experimental Designs" Second Edition, John Wiley and Sons, Inc., New York, 1957.

† Block 1 experimental conditions were run on one Semi-VOST train and Block 2 conditions were run on a second Semi-VOST train.

TABLE 4. COMPARISON OF MEAN SAMPLE AND SURROGATE RECOVERIES FOR BASELINE RUNS AND THE 16 OPERATING CONDITIONS

Test compound	Runs 1 and 2				Sixteen generator operating conditions	
	Sample train recovery, %		Deuterated surrogate recovery,† %		Sample train recovery, %	
	Mean	% CV	Mean	% CV	Mean	% CV
1,1,2,2-Tetrachloroethane	86	13.0	-	-	105	12.6
Pentachlorophenol	0	-	-	-	147	103
Hexachloroethane	85	5.5	-	-	104	7.1
Urethane	67*	9.9	-	-	49	49.9
Pyridine	47	29.1	72	28.1	62	5.2
1,4-Dioxane	91	18.0	85	26.7	102	16.3
Naphthalene	93	4.4	-	-	107	10.7
Chlorobenzene	85	15.0	97	7.1	99	11.3
Toluene	81	13.7	122	13.5	94	29.7
Phenol	87	12.3	108	11.5	86	19.2
Nitrobenzene	87	11.3	102	7.8	111	8.1
Resorcinol	0	-	-	-	3	230

* Does not include Run 2, Train B.

† Surrogates recovered from XAD-2®.

conditions. The water solubility of these two compounds should not be a mitigating factor for their poor recoveries from Runs 1 and 2 since the measurements were taken with no moisture present in the generation system. A recent study[3] reported poor recovery of nitrogen-containing heterocyclic compounds from groundwater extracted with methylene chloride/acetonitrile solvent mixtures. Certain amines will react with methylene chloride in the presence of sodium hydroxide. Therefore, it is possible that pyridine may react during the sample extraction and recovery process. Future experiments are planned to determine why the method produced poor recoveries for several compounds.

The mean recoveries of the baseline study (Runs 1 and 2) were then compared to the means for the 16 generator operating conditions on a compound by compound basis utilizing the "t" statistic. At the 0.01 level of significance, only the means of two compounds (nitrobenzene and hexachloroethane) exhibited a statistical difference (excluding resorcinol and pentachlorophenol). Urethane, pyridine, and resorcinol gave the lowest recoveries in both Runs 1 and 2 and also in the average for the generator experiments. The generator data were evaluated by a comparison between the extremes in operating conditions as given in Table 5. Data resulting from operating condition "cd" should represent the most favorable set of simulation parameters to produce optimal test compound recoveries. With exception of urethane, pentachlorophenol, and resorcinol, test compound recoveries ranged from 72 to 109 percent. Operating condition "ab" can be considered the most challenging set of simulation parameters for the method evaluation since a sample was collected under the conditions of high moisture and NO_x levels with low test compound, sample volume, and flow rate levels. With exception of urethane, pentachlorophenol, resorcinol, and pyridine, test compound recoveries ranged from 71 to 110 percent. These data would indicate that the generator variables generally had no effect on recoveries. Even though pyridine, urethane, and resorcinol exhibited low mean recoveries of 62, 49, and 3 percent, respectively, for the 16 generator operating conditions, these values were not significantly different from the corresponding baseline values of 47, 67, and 0 percent.

TABLE 5. COMPOUND RECOVERIES UNDER GENERATOR CONDITIONS "cd" AND "ab"

Test compound	"cd"* Recovery, %	"ab"† Recovery, %
1,4-Dioxane	104	78
Pyridine	73	41
Toluene	72	84
Urethane	48	40
Chlorobenzene	98	94
1,1,2,2-Tetrachloroethane	109	105
Phenol	81	71
Nitrobenzene	107	110
Hexachloroethane	99	99
Naphthalene	100	95
Resorcinol	0	0
Pentachlorophenol	226	83

* "cd" corresponds to high hydrocarbon concentration; large sample size; low moisture, high SO_2, high HCl; low NO_x; and low sample flow rate.

† "ab" corresponds to high moisture, low SO_2, low HCl; high NO_x; low hydrocarbon concentration; small sample size; and low sample flow rate.

The influence of sample generation variables on test compound recovery was further examined by performing a statistical evaluation of the data presented in Table B-4 (Appendix B). The percentage recoveries for each test compound, excluding resorcinol and pentachlorophenol, were grouped in sets representing Level I and Level II of the sample generation variables. For example, the effect of sample flow rate (variable E) on dioxane recovery was evaluated by aggregating all 1,4-dioxane recovery data into either of two sets representing high or low sample flow rates. An analysis of variance was performed using an F test to determine whether the difference between the two sets was significant. An evaluation of compound recoveries for each level of the sample generation variables indicated that only the NO_x generator variable significantly affected the recovery of certain compounds. At the 99 percent probability value of the F statistic, the mean recoveries for 1,4-dioxane, urethane, and phenol were significantly lower for samples collected at high NO_x (1,000 ppm) levels. Pyridine recovery was also lower at high NO_x levels but the F statistic was significant at only the 84 percent value. The remaining six compounds showed no significant effect of NO_x levels on recovery. Correlation ratios[4] were calculated to provide rough estimates of the proportion of variance in compound recovery accounted for by NO_x. The differences in NO_x generator levels accounted for 38 percent, 26 percent, and 28 percent of the variance in recoveries for 1,4-dioxane, urethane, and phenol, respectively.

Table 6 summarizes the distribution of each of the three affected test compounds throughout the sample train fractions for both levels of NO_x. Compound water solubilities are also presented for comparison. Although the mean recoveries for all three compounds are lower at higher NO_x levels, there are differences between the relative distribution of compound recoveries throughout the sample train fractions. The mean recovery of 1,4-dioxane dropped from 109 percent at Level I to 88 percent at Level II. Although 1,4-dioxane is miscible with water, the XAD-2® sorbent module accounted for nearly two-thirds of the total amount of the compound recovered at either NO_x level. The mean recovery of urethane decreased from 63 percent at Level I to 36 percent at Level II. Unlike 1,4-dioxane, the largest fraction of urethane was found in the sample

TABLE 6. OVERALL RECOVERY AND FRACTIONAL DISTRIBUTION OF 1,4-DIOXANE, URETHANE, AND PHENOL FOR NO_x LEVEL I AND LEVEL II GENERATOR CONDITIONS

Test compound	Solubility in H_2O g/ml @20°C	NO_x generation level*	Mean overall recovery, %	Mean distribution of test compound found within sample train, %		
				XAD-2® sorbent module	Coil rinse	Condensate and impinger contents
1,4-Dioxane	(miscible)	I	109	62	2	36
		II	88	63	5	32
Urethane	2.0	I	63	24	3	73
		II	36	26	17	57
Phenol	0.07	I	97	51	2	47
		II	78	46	12	42

* Level I ≅250 ppm NO_x.
Level II ≅1,000 ppm NO_x.

train condensate and impinger contents. The mean recovery of phenol decreased from 97 percent at Level I to 78 percent at Level II. The distribution of phenol within the sampling train was split almost evenly between the XAD-2® sorbent module and the combined condensate and impinger contents. As NO_x increases from Level I to Level II, overall recovery of the test compounds drops.

A possible explanation for lower compound recovery at high NO_x conditions may involve the formation of artifact compounds through the reaction of HNO_3 with phenol, urethane, and/or 1,4-dioxane in solution. Since the flue gas generation system used air as the makeup gas, a fraction of the nitric oxide introduced in the generator would be oxidized to NO_2 and dissolve in the condensate formed in the Semi-VOST train during sample collection. Phenol is converted by dilute HNO_3 at low temperature to nitrophenols. Urethane will undergo decomposition in the presence of HNO_3. The formation of test compound artifacts was investigated by selecting a number of condensate and impinger sample fractions collected at high NO_x generator conditions and searching the GC/MS data sets for HNO_3 reaction products. No NO_x-related artifacts were found for any of the three compounds. However, the negative finding is inconclusive since suspect artifacts such as nitrophenols are difficult to chromatograph. Further investigations will be conducted to explain the relationship between NO_x levels and 1,4-dioxane, urethane, and phenol sample recoveries. Details of the artifact investigation are provided in Appendix C.

SAMPLE PREPARATION PRECISION AND BIAS EXPERIMENTS

In determining the overall precision and bias of the Semi-VOST procedure, it is instructive to examine each step in the procedure to determine how it will impact the overall method. Consequently, a series of laboratory experiments was conducted to gather data for calculating the precision and bias of the sample preparation and compound analysis steps of the Semi-VOST method. The experiments consisted of: (1) sample concentration only using Kuderna-Danish (K-D), (2) Soxhlet extraction with concentration by K-D, and (3) liquid acid/base extraction with concentration by K-D. The analyses were performed by GC/FID equipped

with an autosampler to minimize sample injection variability. Toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane were selected for this study based on their demonstrated collection and extraction efficiency from XAD-2® and their chromatographic properties. A detailed discussion of these experiments and the statistical calculations are presented in Appendix D. Water-soluble POHCs were not included in the investigation but are being studied separately in order to evaluate and possibly improve compound recoveries from aqueous sample train fractions.

Experimental Description

The laboratory experiment was divided into three series of runs. The first series was designed to determine the precision and bias of the Kuderna-Danish (K-D) concentration step and involved analysis of known samples that had been concentrated by the K-D method. The second series was designed to determine the precision and bias of the K-D concentration step in combination with XAD-2® resin extraction. For these experiments, known sample concentrations were first spiked onto XAD-2® resin, extracted with methylene chloride, and then concentrated by the K-D method. The third series was designed to determine the precision of the K-D concentration step in combination with water extraction to simulate the impinger water sample in the Semi-VOST apparatus. Known samples were spiked into water, acidified and extracted, basified and extracted, with the combined extracts K-D concentrated.

Sixteen analyses were performed for each series. For the first series, each of four individual K-D concentrations was followed by quadruplicate analyses. For the second series, four XAD-2® resin samples were extracted in parallel, extractions and K-D concentrations were performed for each apparatus, and analyzed in quadruplicate. The third series used four water samples, which were both acid and base extracted. K-D concentrations were performed on each water sample extract, and quadruplicate analyses were performed on each K-D concentrate.

Additional sample concentration subsequent to K-D can be achieved utilizing an inert gas to evaporate excess solvent. To determine if compound losses would occur during the step, an experiment was performed by spiking four solutions with the three compounds into 5 mL of methylene

chloride. The solutions were analyzed by GC/FID with an autosampler, concentrated to 2.5 mL, and reanalyzed. These experiments showed no compound losses and are discussed further in Appendix D.

Summary of Results

Table 7 summarizes the laboratory sample preparation precision and accuracy determinations. Accuracy is reported in terms of percentage recovery of each compound and percent bias. For Series 1 autosampler and manual injections and Series 2, the percent recoveries range from 89.5 to 110 percent. There was no bias associated with the K-D concentration step for the three compounds studied. Comparison of results from autosampler injections for Series 1 and 2 indicates lower recoveries when the resin extraction is combined with the K-D concentration step. A bias of -7.9 percent measured for toluene may be related to extraction losses due to its boiling point of 110°C. For Series 3, the percent recoveries are significantly lower than from Series 1 and 2, ranging from 56.1 to 84.3 percent with toluene exhibiting the largest bias of -43.9 percent. Since each step of the sample preparation procedure can introduce method bias, surrogate standards should be added to all sample train fractions to improve the accuracy of calculated compound recovery.

The last two columns in the table give the GC/FID analytical precision and the sample preparation precision, respectively, in terms of their coefficients of variation (% CV). Further details of the calculation of the results given in Table 7 are given in Appendix D. The analytical percent coefficients of variation for Series 1, 2, and 3 (all of which used an autosampler) average 0.8 percent with little variability within or between the test series (with the exception of toluene in Series 2 and chlorobenzene in Series 3). A comparison of the analytical precision results for Series 1 with the autosampler injections to the results for Series 1 with manual injections indicates that the latter percent CV results average over twice those for the autosampler injections, reflecting an operator-related variance component.

TABLE 7. LABORATORY SAMPLE PREPARATION PRECISION AND BIAS DETERMINATION

	Accuracy		GC/FID analytical, % CV	Sample preparation, % CV
	Recovery, %	Bias, %		
Series 1, Autosampler Injections (AsI), K-D Concentration + Analysis				
Toluene	102.0	+2.0	0.73	4.07
Chlorobenzene	106.0	+6.0	0.71	3.30
1,1,2,2-Tetrachloroethane	110.0	+10.0	0.78	3.56
Series 2 (AsI) XAD-2® Extraction, K-D Concentration + Analysis				
Toluene	92.1	-7.9	1.36	1.76
Chlorobenzene	101.0	+1.0	0.77	1.88
1,1,2,2-Tetrachloroethane	105.0	+5.0	0.80	2.06
Series 3 (AsI), Separatory Funnel Extraction, K-D Concentration + Analysis				
Toluene	56.1	-43.9	0.71	8.90
Chlorobenzene	64.2	-35.8	0.91	8.61
1,1,2,2-Tetrachloroethane	84.3	-15.7	0.66	7.74
Series 1, Manual Injections, K-D Concentration + Analysis				
Toluene	89.5	-10.5	2.10	4.03
Chlorobenzene	97.7	-2.3	1.48	3.22
1,1,2,2-Tetrachloroethame	103.0	+3.0	1.14	2.69

For the same comparison of manual and autosampler injections, the sample preparation percent CV results are quite comparable because the variability of the sample preparation should be independent of the injection mode into the analytical apparatus.

A comparison of the sample preparation percent CVs and bias for Series 1, 2, and 3 shows the results for Series 3 to be considerably poorer than for Series 1 and 2. This result reflects the inherent increased variability and bias of the extraction procedure in the separatory funnel extraction for two reasons: (1) the transfer of an organic compound from the water phase to the organic phase is highly dependent on solubility, contact time, and degree of mixing; and (2) manual separation of the phases in a separatory funnel is difficult to reproduce. Future experiments will be conducted to determine if multiple separatory funnel extractions improve sample preparation precision and reduce bias.

For Series 2, the sample preparation percent CVs are less than the sample preparation percent CVs for Series 1 autosampler injections. Because the sample preparation percent CV for Series 2 includes XAD-2® extraction and K-D concentration steps while the sample preparation percent CVs for Series 1 includes only K-D concentration step, the total variability of the sample preparation steps of Series 2 must be at least as large as and probably greater than the variability of the sample preparation step for Series 1. A statistical test of the hypothesis that the standard deviations and sample means (from which the percent CVs are calculated) of Series 1 and 2 (autosampler injection) are equal indicates that there are no differences in the means or standard deviations at the 0.05 and 0.01 levels of significance.

SECTION 6
FIELD EVALUATION

Following completion of the laboratory studies, a field test program was conducted to evaluate method performance at an operational hazardous waste incineration facility. A test plan was prepared which included the collection of a matrixed sequence of samples for the evaluation of:

- method precision,
- bias, and
- POHC sample train breakthrough.

FIELD TEST SITE DESCRIPTION

The field experiments were conducted at Trade Waste Incineration, Sauget, Illinois. The incinerator is designed to destroy hazardous industrial waste other than PCBs and dioxins by combustion at temperatures in the 982-1,093°C range. Typical waste feed materials include:

- organic solvents,
- organic sludges and slurries, and
- solid hazardous materials.

The gases discharged from the combustion chamber pass through a venturi and into a packed scrubber where ammonia is added to neutralize HCl generated from the incineration of chlorinated wastes. A demister is used to coalesce entrained scrubber droplets before the gas stream is exhausted through a stack outfitted with a test platform and sample ports. Details of the process description and plant operation during sample collection are given in Appendix E.

EXPERIMENTAL DESIGN AND SAMPLE COLLECTION

The test program was designed around the use of four simultaneously-operated Semi-VOST trains connected to a common fixed probe sampling stack gases at a point of average velocity. The bias of the method was determined from test samples collected using trains fitted with a dynamic spiking apparatus. Evaluation of the laboratory generator test data indicated that compounds which were collected predominantly on the XAD-2® sorbent modules exhibited the highest recoveries over the range of generator test conditions. Three of the test compounds with good adsorption and recovery from XAD-2® included toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. Single component cylinder gas standards were obtained containing 8 to 10 ppm levels of each compound in nitrogen. The cylinders were manifolded through a series of mass flow controllers to provide a continuous three component gas stream metered into two simultaneously operating trains. The configuration of the dynamic spiking apparatus is shown in Figure 1. The flow controllers were adjusted to provide an equivalent of 10 MDL of each component which would be continuously spiked through a glass "tee" inserted in front of the condenser coil over a 2-hour sample collection period.

Prior to the field test, a laboratory performance evaluation of the system demonstrated that 2-hour dynamic spikes of the test compound mixture into the Semi-VOST train yielded recoveries of 91, 81, and 85 percent for toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane, respectively. Therefore, overall method bias could be determined in a field study by comparing the recoveries of test compounds with the corresponding 10 MDL dynamic spikes.

Method precision was evaluated by determining the mean coefficient of variation for measured differences between levels of identical stack components collected by a series of paired, unspiked trains. The extent of the precision estimates was dependent upon the number of identical compounds that could be identified in a sufficient number of the sample pairs.

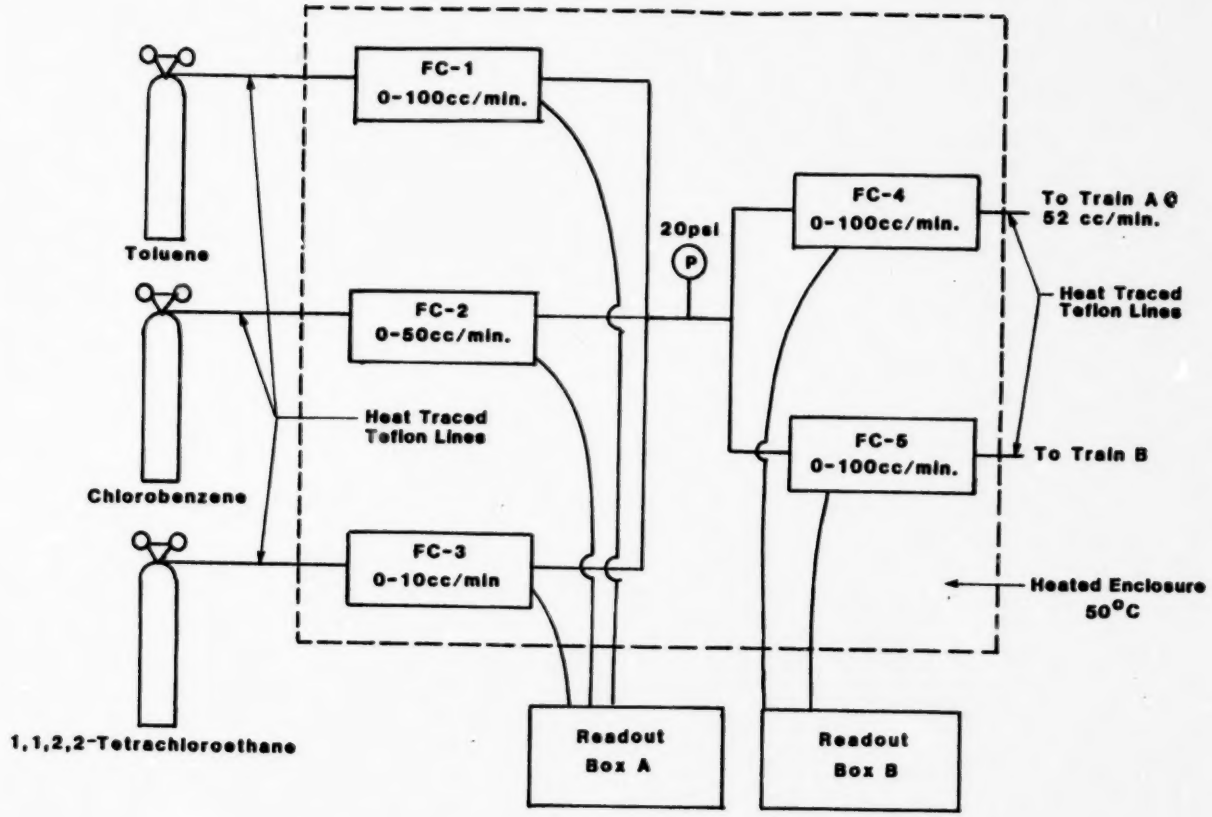

Figure 1. Dynamic spiking apparatus.

Retention of semi-volatile organic incinerator emission components within the sample train was evaluated through a series of distributive volume experiments which were designed to explore the potential for breakthrough of POHCs from the XAD-2® sorbent module. Breakthrough of compounds from the module into subsequent train components increases the potential for sample losses. During an experimental series, each of the four trains was operated at the same sample flow rate. However, two of the four trains were allowed to sample for twice the time of the other two. If breakthrough did not occur, the twofold increase in time at a constant sampling rate should result in a similar increase in the amount of sample collected on a compound by compound basis assuming the source was constant in emissions. The sample collection matrix and testing schedule are given in Table 8.

Two complete trains were assembled to serve as blanks for the test. The train components were chosen at random from the sets of glassware that were shipped to the site. The train was brought to the sampling location and leak checked before and after a run. Blank trains were disassembled along with the test trains. In addition, two separate XAD-2® modules were taken to the test site as trip blanks. Field samples were collected in February 1985.

LABORATORY ANALYSIS

For each train, six individual components were recovered and returned to the laboratory for analysis. The entire population of sample fractions was reviewed to determine an optimal selection of fractions for analysis which would provide data for the evaluation of field test objectives. Since the dynamic spiking experiments were specifically designed to exclude particulate/test compound interactions to permit comparison of field data with laboratory generator results, the particulate filter fractions were archived for later investigation. All sorbent module fractions were included for analysis.

The stack component concentration differences from sorbent fractions representing paired, unspiked trains would provide precision estimates. Table 9 presents a summary of laboratory identification numbers of samples selected for analysis. One of the distributive volume experiments, Run 3-D had a high sample collection volume and, therefore,

TABLE 8. SAMPLE COLLECTION MATRIX AND TEST SCHEDULE

Sample collection matrix*

	Trains A and B	Trains C and D
Run 1	Dynamic Spike	Unspiked
Run 2	Dynamic Spike	Unspiked

	Trains A and C	Trains B and D
Run 3	2h Sample	4h Sample
Run 4	1h Sample	2h Sample
Run 5	1h Sample	2h Sample

Test Schedule

Day 1 - Set up

Day 2 - Runs 1 and 2

Day 3 - Sample recovery

Day 4 - Run 3

Day 5 - Sample recovery

Day 6 - Runs 4 and 5

Day 7 - Sample recovery and equipment teardown

* All trains operated at a sampling rate of 0.014 $m^3 min^{-1}$.

TABLE 9. SAMPLES SELECTED FOR ANALYSIS

Run #	Probe rinse	Filter	XAD-2®	Coil rinse	Condensate and rinse	Impinger and rinse
1-A*	8259	-	8261	8262	8263	8264
1-B*	8265	-	8267	8268	8269	8270
1-C	-	-	8273	-	-	-
1-D	-	-	8279	-	-	-
Blank-1	8283	-	8285	8286	8287	8288
2-A*	-	-	8291	-	-	8294
2-B*	-	-	8297	-	-	8300
2-C	-	-	8303	-	-	-
2-D	-	-	8309	-	-	-
3-A	-	-	8315	-	-	-
3-B	-	-	8321	-	-	-
3-C	-	-	8327	-	-	8330
3-D	-	-	8339	-	-	8342
Blank-3	-	-	8333	-	-	-
4-A	-	-	8345	-	-	-
4-B	-	-	8351	-	-	-
4-C	-	-	8357	-	-	-
4-D	-	-	8363 & 8367	-	-	-
5-A	-	-	8370	-	-	-
5-B	-	-	8376	-	-	-
5-C	-	-	8382	-	-	-
5-D	-	-	8388	-	-	-
RTI spike	-	-	9010	-	-	-
RTI spike	-	-	9011	-	-	-
RTI lab blank	-	-	9012	-	-	-
RTI lab blank	-	-	9013	-	-	-
RTI trip blank	-	-	8397	-	-	-
RTI trip blank	-	-	8398	-	-	-

* Trains which were used with dynamic spiking apparatus.

the greatest potential for breakthrough. The impinger contents from 3-D were selected from the sample fractions for comparison with Run 3-C. In addition, six XAD-2® modules supplied by the Research Triangle Institute were analyzed. Two of these test samples had been spiked with toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. The remaining four were used as blanks: two trip blanks and two laboratory blanks. A total of 45 individual sample fractions were solvent-extracted and analyzed by GC/MS. Results are reported in Appendix F.

A mixture of eight surrogate compounds, listed in Table 10, was selected for sample fraction spikes. A 100-µL aliquot of the surrogate mixture prepared in methylene chloride was added to each sample prior to extraction. The surrogate concentrations in the mixture were selected so that the 100-µL spike would contain a surrogate level equivalent to 10 MDL in a final sample extract volume of 5 mL.

Extracted samples were analyzed on a Finnigan 5100 gas chromatograph/mass spectrometer/data system. A five-point calibration curve was prepared in triplicate using the eight surrogate spiking compounds and the three target compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) at solution concentrations of 10, 25, 50, 100, and 200 ng/µL. Details of GC/MS calibration and instrument conditions are found in Appendix F.

ANALYTICAL RESULTS AND DISCUSSION

Table 11 lists the mean overall surrogate recoveries for all sample media. Mean values range from 75 to 124 percent with coefficients of variation ranging from 14 to 46 percent. Recoveries of all of the surrogates were poorer from liquid media than from the XAD-2® resin, consistent with the results from the laboratory generator experiments. For example, mean recoveries of deuterated toluene and deuterated chlorobenzene from liquid sample fractions were 64 and 77 percent, respectively, when using one extraction. Corresponding recoveries from XAD-2® fractions were 83 and 91 percent, respectively. The recovery measured for ^{13}C-labeled pentachlorophenol is suspect because the coefficient of variation was high for both liquid and XAD-2® fractions,

TABLE 10. SURROGATE SPIKING COMPOUNDS

Compound	Boiling point, °C	10 MDL concentration, ng/μL*
1,4-Dioxane-d_8	102	69.8
Pyridine-d_5	115	85.1
Toluene-d_8	110	18.5
Chlorobenzene-d_5	132	3.7
Phenol-d_5	182	44.8
Nitrobenzene-d_5	211	10.9
Naphthalene-d_8	217	3.2
Pentachlorophenol-$^{13}C_6$	310	4.3

* Concentration of the surrogates in the final extraction volume of 5mL methylene chloride.

TABLE 11. OVERALL SURROGATE RECOVERIES FROM ALL MEDIA

Surrogate compound	Mean* recovery, %	Coefficient of variation, %
d_8-1,4-Dioxane	86.6	17.1
d_5-Pyridine	82.3	23.7
d_8-Toluene	75.0	26.4
d_5-Chlorobenzene	85.5	22.2
d_5-Phenol	96.1	13.6
d_5-Nitrobenzene	117	16.9
d_8-Naphthalene	106	15.8
$^{13}C_6$-Pentachlorophenol	124	46.3

* Mean of 39 values.

which would be associated with variance in the chromatography of the compound. Individual sample fraction surrogate recoveries are tabulated in Appendix F.

Method Bias Determination

Table 12 presents a summary of the analytical results of the dynamic spiking runs for a measure of method bias. For toluene, spiked recoveries varied between 75 and 111 percent. However, the detection of toluene in the probe rinses and coil rinses for Runs 1A, 1B, and the Train Blank was interpreted as either contamination of the sampling trains by fugitive toluene emissions or solvent solution contamination. The latter possibility was investigated by analyzing portions of the methylene chloride and methanol solvents which were returned from the field test. Toluene was not detected in the methanol. However, toluene was found in the methylene chloride at a level of 3.5 ng/μL when corrected for the 50:50 volumetric ratio of methylene chloride to methanol solution used for the coil and condensate rinse solutions in Runs 1 and 2. After elimination of the coil rinse toluene contribution, adjusted spike recoveries were 55 and 94 percent for Runs 1A and 1B, respectively. The mean recovery across Runs 1 and 2 was 87 percent which compares favorably with the corresponding mean recovery for toluene of 92 percent from the laboratory generator study and 91 percent from the laboratory baseline performance test of the dynamic spiking system. After adjustment for deuterated surrogate recoveries, the mean recovery of toluene across Runs 1 and 2 was 101 percent. However, these results are considered tentative until additional sample fractions are analyzed from the two runs to confirm the presence of solvent contamination as the source of toluene in the rinse fractions.

For chlorobenzene, the dynamic spike concentration was low relative to the unexpected high levels measured in the stack gas. Therefore, the resulting small concentration differences between spiked and unspiked samples prevent a realistic estimate of recovery for calculating bias.

The recoveries of 1,1,2,2-tetrachloroethane ranged from 48 to 96 percent. The target compound was detected in one of three condensate rinses analyzed. Additional sample fractions selected for toluene

TABLE 12. ANALYSES OF DYNAMIC SPIKING RUNS

Run	Compound concentration, ng/μL							Recovery* (%)	Adjusted† recovery (%)
	Probe rinse	XAD-2®	Coil rinse	Condensate and rinse	Impinger and rinse	Total	Target		
Toluene									
1A	9.2	10.1	3.6	ND§	ND	13.7	18.5	74	55
1B	7.0	17.4	3.2	ND	ND	20.6	18.5	111	94
1C		2.4							
1D		ND							
2A		16.0			ND	16.0	18.5	87	
2B		20.4			ND	20.4	18.5	110	
2C		ND							
2D		ND							
Train blank	3.1	ND	3.0	4.0	ND				
Chlorobenzene									
1A	ND	23.8	ND	0.7	ND	24.5	3.7		
1B	ND	28.0	ND	ND	ND	28.0	3.7		
1C		26.1							
1D		22.6							
2A		34.7			ND	34.7	3.7		
2B		60.1			ND	60.1	3.7		
2C		20.3							
2D		20.8							
Train blank	ND	ND	ND	ND	ND				

(continued)

TABLE 12. (continued)

Run	Compound concentration, ng/μL: Probe rinse	XAD-2®	Coil rinse	Condensate and rinse	Impinger and rinse	Total	Target	Recovery* (%)	Adjusted† recovery (%)
1,1,2,2-tetrachloroethane									
1A	ND	1.8	ND	ND	ND	1.8	2.5	72	
1B	ND	2.0	ND	0.4	ND	2.4	2.5	96	
1C		ND							
1D		ND				1.4	2.5	56	
2A		1.4				1.2	2.5	48	
2B		1.2							
2C		ND							
2D		ND							
Train blank	ND	ND	ND	ND	ND				

* Excluding probe rinse.

† Excluding probe rinse and coil rinse.

§ ND = compound not detected at its MDL.

analysis will also be studied for the presence of 1,1,2,2-tetrachloroethane. The average of the paired, spiked recoveries for Run 1 is 84 percent which is in close agreement with the 85 percent average recovery of 1,1,2,2-tetrachloroethane determined from the laboratory evaluation of the spiking system. The average recovery of 1,1,2,2-tetrachloroethane of 52 percent in Run 2 suggests a problem with the dynamic spiking system. During the development and evaluation of the system in the laboratory, several design modifications were incorporated specifically to reduce the time at which all three components reached a mixture delivery equilibrium. 1,1,2,2-Tetrachloroethane was always the last component to reach an equilibrium concentration. The time to reach equilibrium was reduced by heat-tracing the spiking system. The extremely cold ambient temperatures prevalent during sample collection may have been responsible for a malfunction of the heating system. Excluding the data from Run 2, a preliminary estimate of -16 percent bias for 1,1,2,2-tetrachloroethane can be made. Additional laboratory studies are needed to finalize the configuration of the dynamic spiking system for determining method bias under a field sampling environmental condition.

Method Precision Determination

Overall method precision was determined using a pool of paired unspiked sample analyses for chlorobenzene. Table 13 summarizes the chlorobenzene precision results. Columns 2, 3, and 4 present the mean, standard deviation, and the percent CV for the concentrations of samples for the duplicated run pairs shown in Column 1. For comparison, the final three columns in the table show the results corrected for a deuterated spike that was put in the sample train after the completion of the sampling and before the sample preparation step or analysis.

Below the chlorobenzene concentration values for runs 5B-5D are pooled values of the standard deviation, the mean, and the resulting percent CV. Pooled values in the row labeled (a) include all runs with the exception of the run pair 4B-4D. Pooled values in row (b) exclude run pairs 4B-4D, 1A-1B, and 2A-2B. The latter two pairs (runs 1A-1B and 2A-2B) were dynamic spiking runs. The method precision for chlorobenzene is 19.9 percent, uncorrected for surrogate recovery, and calculated from a data set representing seven degrees of freedom.

TABLE 13. CHLOROBENZENE PRECISION RESULTS, FIELD STUDY

Run pair	Concentration, μg/m³			Concentration, μg/m³, corrected for deuterated spike recovery		
	Mean	Std. dev.	% CV	Mean	Std. dev.	% CV
1A-1B	69.9	5.41	7.7	69.2	17.2	24.9
1C-1D	65.8	1.57	2.4	71.2	2.12	3.0
2A-2B	88.8	8.00	9.0	152.2	45.7	30.0
2C-2D	61.2	9.59	15.7	72.0	26.4	36.7
3A-3C	80.8	1.86	2.3	92.6	1.85	2.0
3B-3D	93.7	1.76	1.9	100.2	0.40	0.4
4A-4C	102.6	2.86	2.8	102.2	3.60	3.5
4B-4D*	-	-	-	-	-	-
5A-5C	114.0	44.8	39.3	127.6	1.30	1.0
5B-5D	94.7	2.25	2.4	107.7	4.28	4.0
Pooled						
(a)†	85.7	15.7	18.3	99.4	18.6	18.7
(b)§	87.5	17.4	19.9	96.2	10.3	10.7

* Deleted because of sampling problems.

† Pooled (a) values include all run pairs except 4B-4D.

§ Pooled (b) values do not include 1A-1B, 2A-2B, or 4B-4D.

The method precision for chlorobenzene can be separated into three components - sampling, sample preparation, and GC/MS analysis - in terms of percent of total variance and percent CV for each component. Results are presented in Table 14. For the Analytical Laboratory Precision Evaluation (four preparations with four analyses per preparation) using the GC/MS analytical variance estimate, the overall precision was 11.6 percent in terms of percent CV. Table 14 indicates that if the Analytical Laboratory Precision Evaluation was determined with four preparations and with four analyses per preparation, the percentage of the total variance that would be due to the preparation is 21.6 percent, while the GC/MS analytical variance would be 78.4 percent of the total variance. For the preparations and analyses used in the generator study and in the field study, the number of preparations per sample and analyses per preparation are both one. The preparation variance is 6.4 percent of the total variance, while the GC/MS analytical variance would be 93.6 percent of the total variance. The ratio of these two variances (6.4/93.6) was assumed to be constant for chlorobenzene for the generator study and for the field study.

The overall precision estimates for the generator study and the field study were 11.3 and 19.9 (percent CV), respectively. Sampling variance increased from 11.4 to 78.5 percent of the total variance when comparing the generator studies with the field studies. Percent CV is not additive within a particular study, but percent of total variance is additive.

Distributive Volume Results

Table 15 is a tabulation of results from the distributive volume experiments. In Run 3, chlorobenzene levels measured from the XAD-2® fractions doubled with corresponding increases in sample volume, demonstrating good adsorption, retention, and recovery. Similar behavior is noted for run 4 with exception of 4D which represents a composite of two separate XAD-2® traps. Train 4D experienced mechanical problems during sampling which could account for the discrepancy in the result. During Run 5, samples B, C, and D appear consistent. The apparent high value for sample 5A cannot be explained. After eliminating samples 4D

TABLE 14. APPORTIONMENT OF METHOD PRECISION FOR CHLOROBENZENE

	Analytical Laboratory Precision Evaluation with GC/MS			Generator study		Field study	
	% Total variance*	% Total variance†	% CV*,§	% Total variance	% CV	% Total variance	% CV
Sampling	-	-	-	11.4	3.8	78.5	17.1
Sample preparation	6.4	21.6	2.7	5.7	2.7	1.4	2.3
GC/MS analysis	93.6	78.4	10.2	82.9	10.3	20.1	8.6
Overall	100.0	100.0	11.6	100.0	11.3	100.0	19.9

Assumptions:

- GC/MS analytical variance from MDL study applicable in these studies.
- GC/MS instrument response linear function of composition.
- GC/MS sample variance linear function of composition.
- (Sample preparation variance/GC/MS analytical variance) = constant for p = 1, n =1.

* Number of preparations, p = 1; number of analyses per preparation, n = 1.

† Number of preparations = 4; number of analyses per preparation = 4.

§ % CV is percent coefficient of variation = $(s_x/\bar{X}) \times 100$.

TABLE 15. ANALYSES OF DISTRIBUTIVE VOLUME RUNS

Run	Sample volume (m^3)	Chlorobenzene µg	Toluene µg	1,1,2,2-Tetrachloroethane µg
3A	1.48	118	10	ND
3B	2.91	270	37	ND
3C	1.51	124	13	ND
3D	2.69	255	35	ND
4A	0.99	100	ND	ND
4B	1.73	188	11	ND
4C	1.01	106	ND	ND
4D	1.70	97	ND	ND
5A	0.91	132	10	ND
5B	1.71	165	13	ND
5C	0.91	75	ND	ND
5D	1.65	154	12	ND
Train blank	-	ND	ND	ND

and 5A, the remaining data were pooled and plotted in Figure 2 to test the linearity between the chlorobenzene concentration measured and the volume of flue gas sampled. A least squares analysis was performed and the variables were found to be correlated ($r = 0.98$) with a "zero" sample volume intercept for chlorobenzene of -8.8 µg. Therefore, no breakthrough would be predicted. The absence of breakthrough was supported by the analysis of the impinger rinse from Run 3.

Toluene was present in two-thirds of the distributive volume samples. During Run 3, paired values for identical volumes are consistent but the concentration increase is well above the 100 percent theoretical value when accounting for volume differences. Where measured, toluene values are invariant for the remaining runs. Therefore, additional sample fractions will be selected from Runs 3 through 5 for analysis and comparison with similar fractions from Runs 1 and 2.

1,1,2,2-Tetrachloroethane was not detected in any of the distributive volume samples. Appendix F contains GC/MS data representing both qualitative and semi-quantitative results for a number of compounds detected in various sample fractions in addition to the three target compounds. Additional analysis of this data set will be conducted to determine if certain compounds can be associated with the distributive volume experiments to evaluate breakthrough for other hydrocarbons. Future field method evaluations should include the provision for spiking the waste feed with pre-determined POHCs to generate a flue gas stream with a variety of compounds which can be used for method precision determinations and distributive volume experiments.

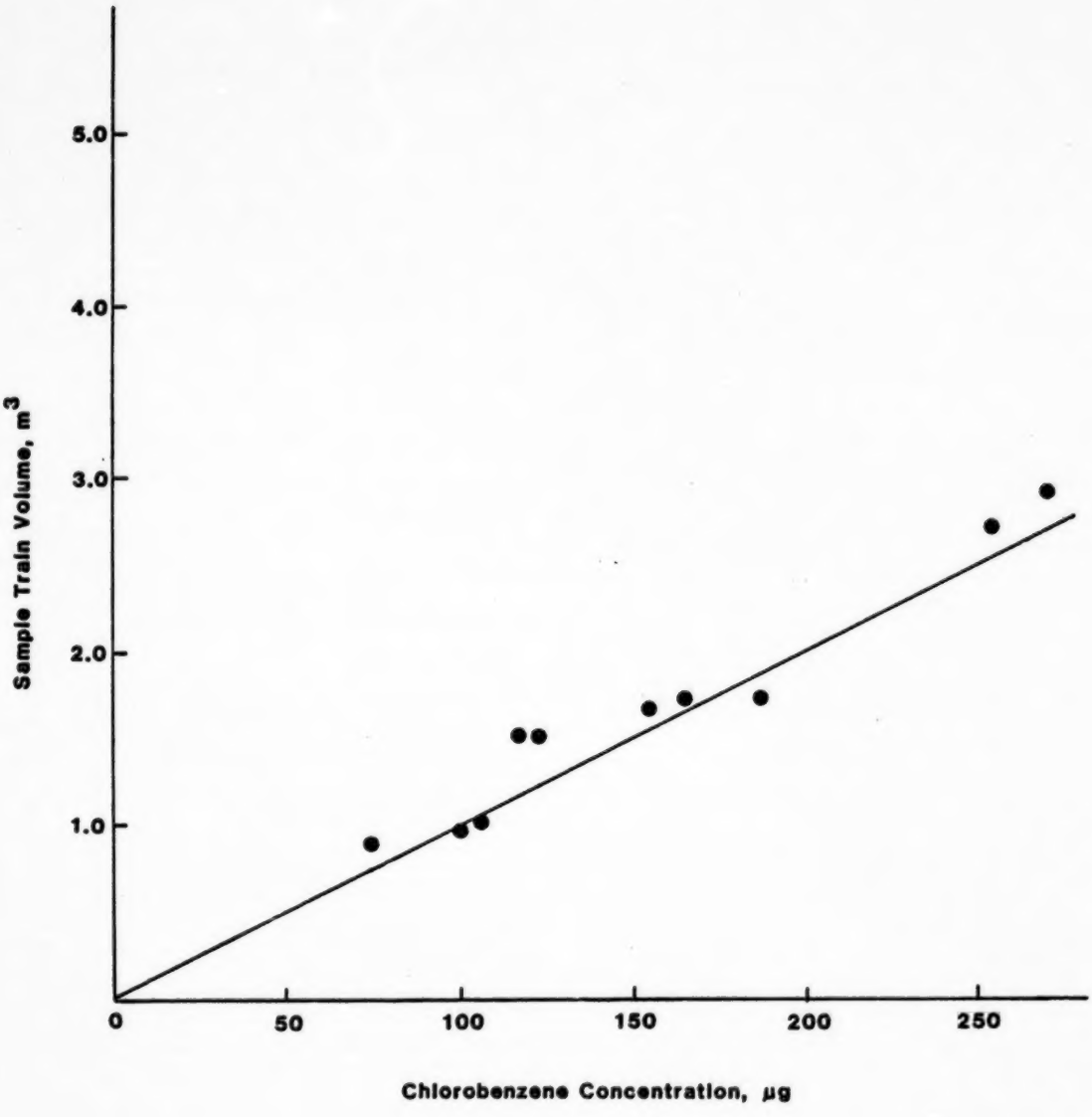

Figure 2. Distributive sample volumes versus chlorobenzene concentration.

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